Azides

Polyazide Chemistry: The First Binary Group 6 Azides, $Mo(N_3)_6$, $W(N_3)_6$, $[Mo(N_3)_7]^-$, and $[W(N_3)_7]^-$, and the $[NW(N_3)_4]^-$ and $[NMo(N_3)_4]^-$ Ions**

Ralf Haiges, Jerry A. Boatz, Robert Bau, Stefan Schneider, Thorsten Schroer, Muhammed Yousufuddin, and Karl O. Christe**

Dedicated to Professor Kurt Dehnicke

Whereas numerous binary transition-metal azido complexes have been reported,[1] no binary Group 6 azides are known. Only a limited number of partially azide-substituted molybdenum and tungsten compounds have been reported.[2–30] Furthermore, no heptaazido compounds have been described.

Herein, we report the synthesis and characterization of the first binary Group 6 azides, $Mo(N_3)_6$, $W(N_3)_6$, $[Mo(N_3)_7]^-$, and $[W(N_3)_7]^-$. The last two ions represent the first examples of heptaazides. We also report the crystal structure of $W(N_3)_6$ and the controlled nitrogen loss from the heptaazido anions to give nitrido-teraazido anions. The $[NMo(N_3)_4]^-$ ion is already known but had been obtained by a different method.[25]

The reactions of MoF_6 or WF_6 with excess $(CH_3)_3SiN_3$ in acetonitrile solution at -25 to $-30\,°C$ result in complete fluoride–azide exchange and yield clear, dark-red solutions of $Mo(N_3)_6$ or $W(N_3)_6$, respectively [Eq. (1), (M = Mo, W)].

$$MF_6 + 6\,(CH_3)_3SiN_3 \rightarrow M(N_3)_6 + 6\,(CH_3)_3SiF \qquad (1)$$

Removal of the volatile compounds (CH_3CN, $(CH_3)_3SiF$, and excess $(CH_3)_3SiN_3$) at $-25\,°C$ results in the isolation of the neat hexaazides in quantitative yield.

As expected for covalently bonded, neutral, high-oxidation-state polyazides,[31] $Mo(N_3)_6$ and $W(N_3)_6$ are extremely shock sensitive and can explode violently even at low-temperature, when either touched with a metal spatula or by rapid change in temperature, such as freezing with liquid nitrogen. $W(N_3)_6$ was isolated as a dark red solid, and ruby-red single crystals were obtained by recrystallization from its CH_3CN solution. Neat $W(N_3)_6$ must be handled with extreme care and at reduced temperature. Warming the compound to ambient temperature results in violent decomposition and can cause serious damage. For example, when a Teflon ampule, containing a small amount of single crystals, was allowed to warm to room temperature inside a stainless steel can, an explosion resulted which not only destroyed the ampule but also blew a hole of 5-cm diameter through the wall of the steel can. $Mo(N_3)_6$ was obtained as a dark red solid. It is even more sensitive than $W(N_3)_6$ and explodes violently upon the slightest provocation, such as a rapid change in the pressure of the inert gas in the vacuum line.

Tungsten hexaazide was characterized by its crystal structure[32] and vibrational spectroscopy. It crystallizes in the trigonal space group $P\bar{3}$ and contains isolated $W(N_3)_6$ molecules (Figure 1), as shown by the closest W···N and N···N contacts between neighboring molecules of 4.02 Å and 2.95 Å, respectively. The structure of the $W(N_3)_6$ unit is only slightly distorted from perfect S_6 symmetry and closely resembles those of $[As(N_3)_6]^-$,[33] $[Sb(N_3)_6]^-$,[34] $[Si(N_3)_6]^{2-}$,[35] $[Ge(N_3)_6]^{2-}$,[36] and $[Ti(N_3)_6]^{2-}$,[1a] but contrasts that of $[Te(N_3)_6]^{2-}$[37] which possesses a sterically active free valence electron pair on its central atom. $W(N_3)_6$ consists of an asymmetric $W(N_3)_2$ unit with two azido groups covalently bonded in a bent fashion to the tungsten. The remaining four coordination positions at the metal center are occupied by four symmetry related azido groups (symmetry operations $-y+1, x-y+1, z$ and $-x+y, -x+1, z$). The observed W–N bonds of 1.949(2) Å and 2.006(2) Å are significantly longer than that of 1.85(2) Å found for $[WF_5N_3]$.[13a]

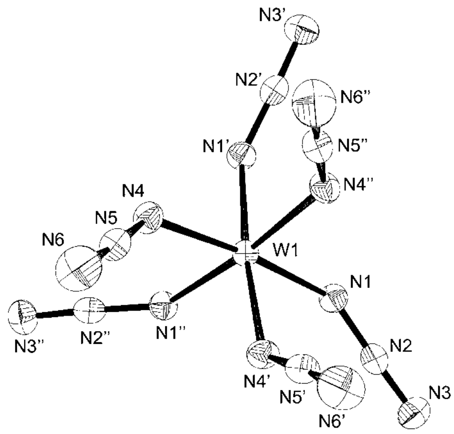

Figure 1. ORTEP diagram of $W(N_3)_6$. Thermal ellipsoids are set at 50% probability. The tungsten atom is situated on a crystallographic site of S_6 symmetry. Selected bond lengths [Å] and angles [°]: W1-N1 1.949 (2), W1-N4 2.006 (2), N1-N2 1.224(2), N2-N3 1.123(2), N4-N5 1.216(2), N5-N6 1.129(2); N1-N2-N3 176.7(2), N4-N5-N6 176.7(2), N1-W1-N1′ 92.42(6), N1-W1-N4 172.84(5), N1-W1-N4′ 94.68(5), N1-W1-N4″ 86.38(6), N4-W1-N4′ 86.69(6), W1-N1-N2 138.31(11), W1-N4-N5 134.34(12).

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14. ABSTRACT
Whereas numerous binary transition-metal azido complexes have been reported,[1] no binary Group 6 azides are known. Only a limited number of partially azide-substituted molybdenum and tungsten compounds have been reported. Furthermore, no heptaazido compounds have been described. Herein, we report the synthesis and characterization of the first binary Group 6 azides, Mo(N3)6, W(N3)6, [Mo(N3)7]- and [W(N3)7]-. The last two ions represent the first examples of heptaazides. We also report the crystal structure of W(N3)6 and the controlled nitrogen loss from the heptaazido anions to give nitrido-teraazido anions. The [NMo(N3)4]- ion is already known but had been obtained by a different method.

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The observed low-temperature Raman spectrum of W-$(N_3)_6$ (Figure 2) was assigned (Supporting Information Table S1) by comparison with the spectra calculated at the MP2[38] and B3LYP[39] levels of theory using a SBKJ + (d) basis set.[40] Although the calculated frequencies and intensities vary somewhat with the method used, their overall agreement with the experiment is very satisfactory. The internal modes of the azido ligands are separated into groups of six, owing to in-phase (one mode) and out-of-phase (five modes) coupling, with the in-phase mode resulting in the highest polarizability change and Raman intensity. For example, the antisymmetric N_3 stretching modes exhibit two very intense bands at 2139 and 2130 cm^{-1}, which represent the in-phase coupled mode, split by either Fermi resonance or site symmetry effects, and a cluster of five less intense bands between 2107 and 2064 cm^{-1} which represents the five out-of-phase coupled modes. The $\{WN_6\}$ skeleton is approximately octahedral with the deviations from right angles being 7° or less. Therefore, the skeletal vibrations can be derived from O_h symmetry, allowing for a splitting into the degenerate components (two for the E modes and three for the F modes). It should be noted that there is no clear preference for using either the MP2 or the B3LYP set for fitting the entire spectrum. There is considerable variation in the relative intensities and sequences of the modes within a given group, and both sets should be used for a comparison with the observed spectrum.

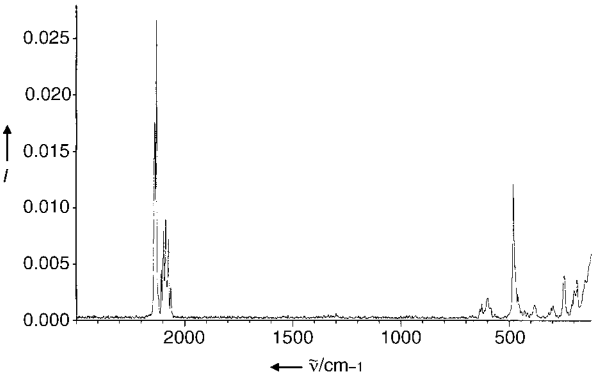

Figure 2. Low-temperature Raman spectrum of solid $W(N_3)_6$.

Because of its extreme sensitivity, the identity of molybdenum hexaazide could only be established by its low-temperature Raman spectrum in CH_3CN solution (Figure 3 and Supplementary Table S2). The agreement between observed and calculated spectra is again satisfactory. All attempts failed to obtain single crystals of diffraction quality. Additional proof for the presence of $Mo(N_3)_6$ was obtained by its conversion into $[Mo(N_3)_7]^-$ and the known[25] $[NMo(N_3)_4]^-$ ion.

The reactions of $M(N_3)_6$ (M = Mo or W) with ionic azides, such as $[NMe_4]^+[N_3]^-$ or $[PPh_4]^+[N_3]^-$, produce the corresponding $[M(N_3)_7]^-$ salts [Eq. (2), (A = PPh_4, NMe_4)].

$$M(N_3)_6 + A^+[N_3]^- \rightarrow A^+[M(N_3)_7]^- \quad (2)$$

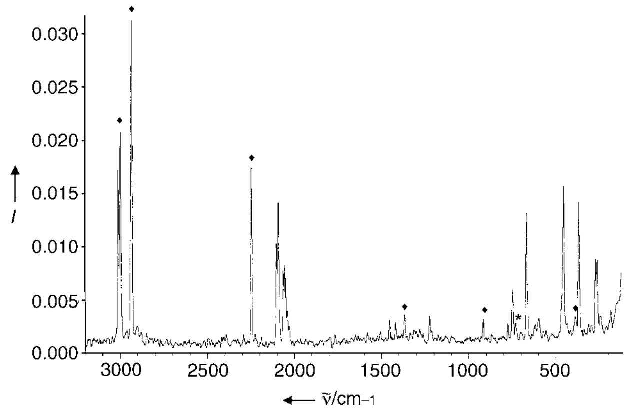

Figure 3. Low-temperature Raman spectrum of $Mo(N_3)_6$ dissolved in CH_3CN. The band marked by an asterisk (*) is due to the Teflon-FEP sample tube. Bands marked by ◆ are from CH_3CN.

Salts of both heptaazido anions were isolated at low temperature as extremely shock-sensitive red solids that explode violently when warmed towards room temperature. Not surprisingly, they are less stable and more difficult to handle than hexaazido salts, thus preventing us from obtaining their crystal structures. These salts were characterized by low-temperature Raman spectroscopy and represent the first known examples of covalent heptaazides. The spectra of $[PPh_4][Mo(N_3)_7]$ and $[PPh_4][W(N_3)_7]$ are shown in Figure 4 and 5, respectively (the observed and calculated frequencies and intensities are listed in the Supporting Information Tables S3 and S4). Three different ligand arrangements are possible for heptacoordinated transition-metal complexes which differ only little in energy.[41] They are derived from a pentagonal bipyramid (1/5/1 arrangement), a monocapped trigonal prism (1/4/2 arrangement), and a monocapped octahedron (1/3/3 arrangement). Therefore, we have explored the possibility of these three arrangements for $[W(N_3)_7]^-$ at the B3LYP(3)/SBKJ + (d) level of theory. Two stable minimum energy structures, a 1/5/1 and a 1/4/2 structure (Figure 6 and Supporting Information), were located, the 1/5/1 structure

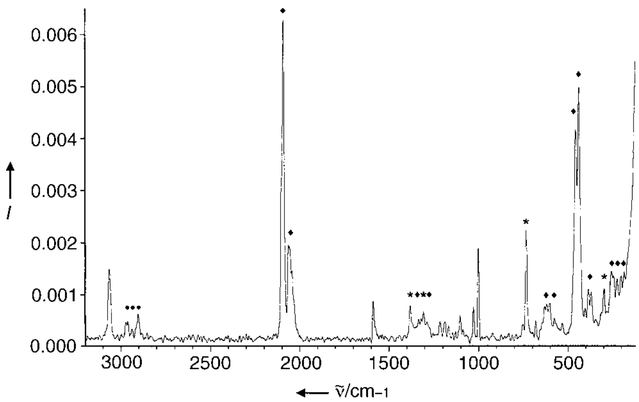

Figure 4. Low-temperature Raman spectrum of $[PPh_4][Mo(N_3)_7]$. The bands marked by an asterisk (*) are due to the Teflon-FEP sample tube. Bands marked by ◆ are from the $[Mo(N_3)_7]^-$ ion. The three bands marked by ● arise from excess Me_3SiN_3.

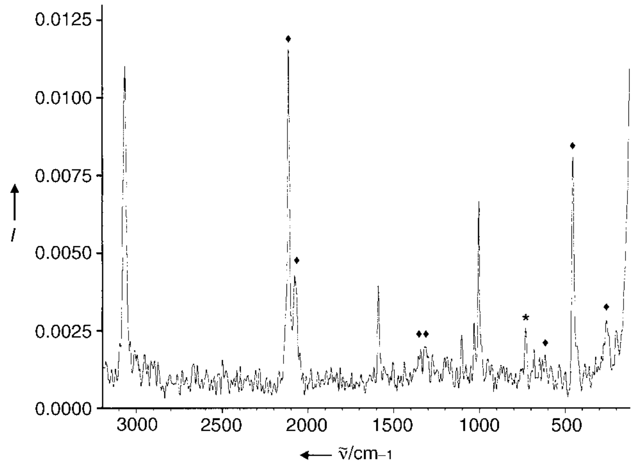

Figure 5. Low-temperature Raman spectrum of $[PPh_4][W(N_3)_7]$. The band marked by an asterisk (*) is due to the Teflon-FEP sample tube. Bands marked by ◆ are from the $[W(N_3)_7]^-$ ion.

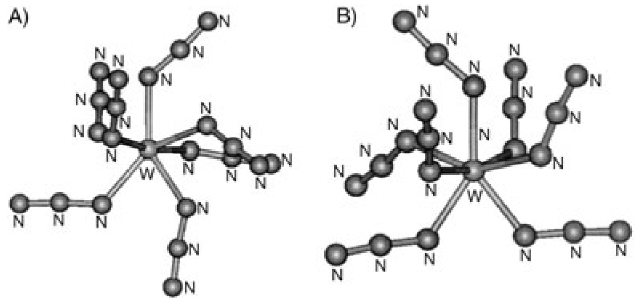

Figure 6. B3LYP/SBKJ+(d) optimized geometries of $[W(N_3)_7]^-$. A) Pentagonal bipyramid (1/5/1), B) monocapped trigonal prism (1/4/2).

being favored by 3.3 $kcal\,mol^{-1}$. When monocapped octahedral structures were used as starting points, the calculations always converged to the pentagonal bipyramidal structure. This result was somewhat unexpected because $[WF_7]^-$ and $[MoF_7]^-$ exhibit monocapped octahedral structures in their cesium salts.[41h] In view of the small energy difference, the similarity of their calculated vibrational spectra, and the sensitivity of the calculated spectra to the level of theory used (Supporting Information Tables S3 and S4), it was not possible to distinguish between the 1/5/1 and 1/4/2 structures based on the observed Raman spectra. Additional evidence for the formation of heptazido anions is derived from the observed frequencies. Compared to the neutral hexaazides, the addition of a negatively charged $[N_3]^-$ ion increases the ionicity of the metal-azide bonds and the ionic character of the azide ligands. This effect should cause decreases in the antisymmetric N_3 ligand and $\{MN_6\}$ skeletal stretching frequencies and increases in the symmetric N_3 ligand frequencies, and is clearly observed in our spectra.

Solutions of either heptaazido anion in SO_2 or CH_3CN decompose on warming to room temperature with nitrogen evolution and formation of the tetraazido nitrido molybdate(VI)[25] and tetraazido nitrido tungstate(VI) anion, respectively [Eq. (3) (M = Mo, W)].

$$A^+[M(N_3)_7]^- \xrightarrow{>-20^{\circ}C} A^+[NM(N_3)_4]^- + 4\,N_2 \quad (3)$$

The $[NW(N_3)_4]^-$ salts can also be prepared in a single step from the corresponding $[WF_7]^-$ salt and $(CH_3)_3SiN_3$ in CH_3CN solution [Eq. (4), (A = PPh_4, NMe_4)].

$$A^+[WF_7]^- + 7\,(CH_3)_3SiN_3 \rightarrow A^+[NW(N_3)_4]^- + 4\,N_2 + 7\,(CH_3)_3SiF \quad (4)$$

The identity of $[NW(N_3)_4]^-$ and $[NMo(N_3)_4]^-$ was established by vibrational spectroscopy and for $[PPh_4][NMo(N_3)_4]$ also by its crystal structure (see Supporting Information, Figure S1 and Supplementary Tables S9–S13).[42] The structure of the $[NMo(N_3)_4]^-$ ion and its vibrational spectra were in excellent agreement with those reported by Dehnicke and coworkers for $[AsPh_4]^+[NMo(N_3)_4]^-$, which was prepared from the $[NMoCl_4]^-$ salt and AgN_3 in a CH_2Cl_2 suspension,[25] and, therefore require no further discussion. The observed Raman spectrum of $[NMe_4][NW(N_3)_4]$ is shown in Figure 7. The observed frequencies and assignments, based on the calculated spectra, are listed for both tetraazido nitrido anions in the Experimental Section.

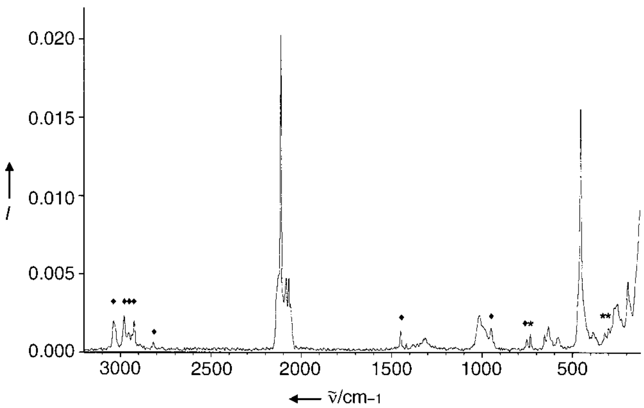

Figure 7. Low-temperature Raman spectrum of $[NMe_4][NW(N_3)_4]$. The bands marked by an asterisk (*) are due to the Teflon-FEP sample tube. Bands marked by ◆ are from the $[NMe_4]^+$ ion.

Experimental Section

Caution! *Covalent azides are potentially hazardous and can decompose explosively under various conditions! The polyazides of this work are extremely shock-sensitive and can explode violently upon the slightest provocation. They should be handled only on a scale of less than 1 mmol and can cause, even on a 1-mmol scale, significant damage. During the handling of $W(N_3)_6$ and $Mo(N_3)_6$, rapid changes in temperature or pressure can result in violent explosions. The use of appropriate safety precautions (safety shields, face shields, leather gloves, protective clothing, such as heavy leather welding suits and ear plugs) is mandatory.[1a]* ***Ignoring safety precautions can lead to serious injuries!***

Materials and Apparatus: All reactions were carried out in Teflon-FEP ampules (FEP = perfluoro ethylene propylene polymer) that were closed by stainless steel valves. Volatile materials were handled in a Pyrex glass or stainless steel/Teflon-FEP vacuum line.[43] All reaction vessels and the stainless steel/Teflon-FEP vacuum line

were passivated with ClF_3 prior to use. Nonvolatile materials were handled in the dry argon atmosphere of a glove box.

Raman spectra were recorded in the range 4000–80 cm^{-1} on a Bruker Equinox 55 FT-RA spectrophotometer using a Nd-YAG laser at 1064 nm with power levels *less(!!)* than 50 mW. Teflon-FEP tubes with stainless steel valves that were passivated with ClF_3 were used as sample containers.

The starting materials WF_6, MoF_6 (both Ozark Mahoning) and $[PPh_4]I$ (Aldrich) were used without further purification. $(CH_3)_3SiN_3$ (Aldrich) was purified by fractional condensation prior to use. Solvents were dried by standard methods and freshly distilled prior to use. $[PPh_4]F$ and $[PPh_4]N_3$ were prepared from $[PPh_4]I$ and AgF and AgN_3, respectively. $[NMe_4][WF_7]$ and $[PPh_4][WF_7]$ were obtained from WF_6 with $[NMe_4]F$ and $[PPh_4]F$, respectively.[44] $[NMe_4]F$[45] and $[NMe_4]N_3$,[46] were prepared by literature methods.

Preparation of $W(N_3)_6$: On the stainless steel vacuum line, WF_6 (0.463 mmol) was condensed at −196 °C into a Teflon-FEP ampule. The ampule was then attached to a glass vacuum line and after evacuation, CH_3CN (50 mmol) was condensed in at −196 °C. The mixture was allowed to warm to ambient temperature forming a colorless solution. After re-cooling to −196 °C, $(CH_3)_3SiN_3$ (4.43 mmol) was condensed onto the frozen solution, and the mixture was warmed to −25 °C. Within minutes, the mixture turned orange-red and the color intensified while the reaction proceeded. After 1 h, the reaction mixture was dark red. All volatile material was pumped off at −25 °C, leaving behind a dark red solid (yield: 0.215 g, expected for 0.463 mmol of $W(N_3)_6$, 0.202 g). Ruby-red single crystals were grown from a solution in CH_3CN by slow evaporation of the solvent in vacuo.

Preparation of $Mo(N_3)_6$: The reaction was carried out as described above for $W(N_3)_6$ using MoF_6 (0.133 mmol), CH_3CN (30 mmol), and $(CH_3)_3SiN_3$ (1.07 mmol). After keeping the mixture for 1 h at −30 °C, a Raman spectrum of the reaction mixture was recorded. The removal of all material volatile at −30 °C resulted in the formation of a dark red, extremely explosive solid.

Preparation of $[M(N_3)_7]^-$ salts (M = Mo, W): Cold solutions of $M(N_3)_6$ (0.20 mmol) in SO_2 (60 mmol) were added to mixtures of PPh_4N_3 (0.20 mmol) and SO_2 (25 mmol) at −64 °C. The mixtures were kept at this temperature for 30 min and occasionally agitated. All volatiles were removed at −64 °C in a dynamic vacuum, leaving behind dark red solids; weight expected for 0.20 mmol of $[PPh_4][Mo(N_3)_7]$: 0.146 g; found 0.158 g; weight expected for 0.20 mmol of $[PPh_4][W(N_3)_7]$: 0.163 g; found: 0.171 g.

Preparation of $[NM(N_3)_4]^-$ salts (M = Mo, W): Cold solutions of the $[M(N_3)_7]^-$ salts (0.25 mmol) in SO_2 (100 mmol) were warmed from −64 °C to −25 °C. After about 30 min at −25 °C, the temperature was raised over a period of 2 h to 25 °C. All volatiles were slowly removed in a dynamic vacuum, leaving behind dark red solids.

$[P(C_6H_5)_4][NMo(N_3)_4]$: weight found: 0.145 g; weight expected for 0.25 mmol: 0.154 g; Raman of the $[NMo(N_3)_4]^-$ ion (50 mW, −80 °C): $\tilde{\nu}$ = 2109(10.0), 2098(2.2), 2070(1.5), 2064(1.9), 2055(1.8), 2047(1.1), 2040(1.1), 2025(0.5) ($\nu_{as}N_3$); 1331(0.7), 1319(0.7), 1285(0.5), 1259(0.3) (ν_sN_3); 1034(2.2) ($\nu Mo\equiv N$); 657(0.6), 639(0.6), 626(0.5), 596(0.4), 589(0.4), 568(0.3) (δN_3); 443(4.1), 429(4.1), 405(0.8), 384(0.9), 357(1.1) (νMoN_{azide}); 292(1.2), 273(1.1), 258(1.5) (δMoN_{azide}); 216(1.2), 183(2.7), 161(1.7) cm^{-1}.

$[N(CH_3)_4][NW(N_3)_4]$: weight found: 0.117 g, weight expected for 0.25 mmol: 0.110 g; Raman of the $[NW(N_3)_4]^-$ ion (50 mW, −80 °C): $\tilde{\nu}$ = 2114(10.0), 2083(2.2), 2069(2.2), 2060(1.4), ($\nu_{as}N_3$); 1324(0.4), 1315(0.4), 1259(0.2) (ν_sN_3); 1010(1.0), ($\nu W\equiv N$); 655(0.6), 632(0.7), 611(0.3), 579(0.5) (δN_3); 452(7.1), 416(0.7), 321(0.6) (νWN_{azide}); 266(1.3), 262(1.3), 253(1.4), 247(1.4), 226(1.0) (δWN_{azide}); 189(2.0), 118(4.0), 110(4.0), 100(4.1) cm^{-1}.

Theoretical Methods: The molecular structures and harmonic vibrational frequencies were calculated using second-order many-body perturbation theory[38] (denoted as MP2, but also known as MBPT(2)) and also density functional theory (DFT) level using the B3LYP hybrid functional,[39a–c] which included the VWN5 correlation functional.[39d] The Stevens, Basch, Krauss, and Jaisen effective core potentials and the corresponding valence-only basis sets were used.[40a–b] The basis set for nitrogen was augmented with a d polarization function (exponent of 0.8[40c]) and a diffuse s+p shell (exponent of 0.0639[40d]), denoted as SBKJ+(d). Hessians (energy second derivatives) were calculated for the final equilibrium structures to determine if they are minima (positive definite hessian) or *n*th-order transition states ("*n*" negative eigenvalues). All calculations were performed using the electronic structure code GAMESS.[47]

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